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Study of Fe(III)-NTA chelates stability for applicability in photo-Fenton at neutral pH

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ABSTRACT

The stability of ferric nitrilotriacetate chelates (Fe(III)-NTA) was studied under thermal, oxidative and photochemical stress. The knowledge of chelate stability is fundamental to correctly implement the management system of wastewater treatment plant for application of chelates as catalyst in photo-Fenton process at neutral pH. Fe(III)-NTA solution stability was monitored under different temperature conditions ($T = 10–30\,^{\circ}C$), in presence and absence of UV-A irradiation and by adding three different concentrations of H_2O_2. The additional effect on chelate stability caused by different irradiation source (UV-A, UV-C and Xenon lamps) was also evaluated. Although the complexes were stable under the temperature test range, temperature control is crucial when stressing the solution by irradiation or by adding hydrogen peroxide. The solution was kept stable during two hours of reaction under UV-A irradiation only when temperature was set at 10–15 °C while in presence of hydroxyl radicals ($HO^{\bullet}$) the temperature control could only reduce the chelates decomposition. Fe(III)-NTA solution mineralization could be obtained under irradiation and radical strain. Thus, the production of organic radical from free ligands was also demonstrated. Finally, the suitableness of UV-C lamps as light source for the process application was questioned since they caused a strong degradation of the chelate solution. Indeed, only 30 min of UV-C irradiation by adding 0.59 mM of hydrogen peroxide caused almost 90% reduction of the chelate content in the solution.

1. Introduction

Nitrilotriacetic acid (NTA) belongs to the family of aminopolycarboxylic acids (APCAs) characterized by compounds distinguished by several carboxylate groups linked through carbon atoms to one or more nitrogen atom. These APCAs have the ability to form very stable water-soluble complexes with many metallic di- or trivalent ions. Due to their remarkable complexation properties, synthetic APCAs have been used for domestic and industrial applications to control the solubility and precipitation of metallic ions [1,2].

NTA has been extensively used in a variety of industrial applications. Moreover, in the last years, chelating agents are being also considered a useful option to perform water treatments as photo Fenton like at neutral pH in order to form photoactive species ($Fe^{3+}L$) and then keep iron soluble in a wider range of pH than of conventional treatment [3,4]. It is generally known as advanced oxidation processes (AOPs) are recognized wastewater treatments able to produce non-selective radical species that oxidize a wide range of recalcitrant compounds. Among them, photo-Fenton process is one of the most effective treatments that substantially improve the efficiency obtainable by conventional Fenton. Fenton oxidation process is based on the catalytic reaction of H_2O_2 with iron ions [5] with following production of $HO^{\bullet}$ radicals [6]. Thus, photo-Fenton process is basically the combination of Fenton reagents and UV–vis radiation (λ <600 nm). The photo-reduction of Fe^{3+} to Fe^{2+} ions for $\lambda < 580$ nm [7] and the photolysis of H_2O_2 via shorter wavelength ($\lambda < 310$ nm) ensures, in fact, extra $HO^{\bullet}$ radicals production. The effectiveness of photo-Fenton process have been already demonstrated as summarized in several reviews [8]. However, its application is reduced by the high operational costs related to the influent acidification and subsequent neutralization. The discharge of acidic effluent is, in fact, absolutely forbidden in order to preserve the aquatic fauna from the risk of making uninhabitable the environment of life. Moreover, additional costs are produced when, after neutralization, a great amount of sludge is produced. In fact, the necessity of separating and treating the sludge generated considerably increases the costs and the complexity of the

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treatment making the process not suitable for real application. Thus, the possibility of treating without prior adjustment of the pH could increase the use of photo-Fenton for wastewater treatment. In this regard, the scientific community is getting involved in an additional renovation of the treatment using organic substances able to keep iron soluble at circumneutral pH (photo-Fenton like).

Several compounds have been largely considered as potentials iron chelators in photo-Fenton like processes at neutral pH [3,9–11]. Even though most of the chelating agents studied over the years are able to be used as iron chelators, several are the concerns of the faith related to their usage. The eventually poor biodegradability and the increase of toxicity due to the formation of complexes with heavy metals should be carefully evaluated. Thus, it is important avoiding pollute the environment and increase the toxicity of the effluent to keep iron soluble for the treatment.

The strong ability of NTA as iron chelator represented by its stability or equilibrium constant (pK = 15.9 for Fe(III)-NTA complexes) makes it a reasonable candidate to be employed in this process [12,13]. Together with the strong ability of the NTA as iron chelator, its higher biodegradability compared to other strong chelator as well as its supposed good stability under irradiation make this compound particularly competitive in its usage [14,15]. The biodegradability of NTA as free chelator has been already demonstrated and the concern related to the fate of NTA release in the environment after treatment can be almost denied. The presence of a great variety of NTA-degrading microorganism in most environmental compartment has been in fact demonstrated [2]. Moreover the worry about the toxicity of NTA has been also disproved especially if compared to other chelating agents such as EDTA and if considering the low concentration hypothesized for its application. Sillanpää et al. (2003), in fact, carried out a study in which the acute toxicity of some chelates was analyzed. The toxicity as LC_{50} and EC_{50} of NTA was calculated and a very low toxicity exhibited by NTA was showed. However, the toxicity and the biodegradability of the chelates are strongly dependent on the metal speciation [16,17]. On certain occasion, the toxicity of the chelate can be even lower than of the free chelator. In presence of Mn-NTA an enhancement in the algal growth was in fact also observed [17]. Perhaps an increment of the acute toxicity can be expected in case of heavy metal chelation. Nevertheless, considering the higher value exhibited by the equilibrium constant of Fe-NTA chelates, the exchange of iron for others heavy metals might be underdog.

The efficiency of Fe(III)-NTA as photo-Fenton like catalyst has been already demonstrated in previous study [10]. Nevertheless, the durability of chelate stability over reaction is fundamental in order to better perform the treatment and to make it competitive in water decontamination compared with others advanced oxidation processes (AOPs). To the best of our knowledge, there is no study dealing with the stability of Fe(III)-NTA considering its use as iron chelator in photo-Fenton at neutral pH.

The catalytic activity of the chelates is strongly dependent of their stability. In fact, the pH operating condition (circumneutral pH) makes impossible to keep soluble the iron content if released from the chelators structure. Chelates decomposition should be avoided not only in order to elude the reaction rate decrease but also to prevent large amount of $Fe(OH)_3$ concentrated waste. In fact, as already discussed in the case of conventional photo-Fenton, a great amount of iron precipitate would mean the necessity of providing the plant of an additional unit for sludge separation. Thus, the knowledge of the influence of the operating condition adopted for photo-Fenton at neutral pH is absolutely important to predict the efficiency of the treatment. Furthermore, the control of the parameter set up is really important to extend the chelates lifetime until the achievement of the required level of quality.

Ferric nitrilotriacetate Fe(III)-NTA, whose absorption spectrum shows a tail up to the visible domain, will undergo transformation upon irradiation (especially when adding oxidants species into the solution). In this regard, it is of great importance to have a thorough understanding of the chelate solution behavior under UV light irradiation [18]. The monitoring of the spectrum modification over reaction can supply useful information if overreaction instability phenomena will arise. In fact, the absorbance of the solution in correspondence of the spectrum peak has been demonstrated to be directly proportional to the chelates concentration. Thus, peak reduction over time represents a clear sign of the complexes breakage and subsequent decrement of the catalyst content.

The aim of this paper is to study the stability of Fe(III)-NTA chelates by monitoring the absorption spectrum during the reaction under different operating conditions. Various factors have been taken into account as source of irradiation, the presence of oxidants as well as the effect of aging and temperature. The entire study was performed at neutral pH.

2. Materials and methods

2.1. Reagents

Chemicals used as catalysts (anhydrous iron(III) chloride ($FeCl_3$)), oxidants (hydrogen peroxide solution (H_2O_2), 30% w/v), hydrochloric acid (HCl), auxiliary chemicals for initial pH value adjustment (sodium hydroxide (NaOH)) were purchased from Panreac Quimica (Spain). Chelating agent, nitrilotriacetic acid (NTA) was obtained from Alfa Aesar (Spain).

The filters used were Chmlab Group 0.45 μm (pore size) PVDF membrane filters and Minisart-RC 0.20 μm (pore size) nylon membrane filters.

2.2. Sample preparation

Ferric ion solution 71.63 mM was prepared fresh daily dissolving anhydrous $FeCl_3$ in 0.1 M HCl to minimize iron(III) hydrolysis and polymerization [19]. Iron chelate solution 0.36 mM of Fe^{3+}, was prepared by directly mixing the ferric ion solution with a solution of the NTA in Milli-Q water. Thus, after approximately 15 min of stirring, the pH of solution was slowly adjusted to 8.0 to allow the chelating agent's dissolution. Then it was let stirring during one extra hour to ensure the complete chelation of iron content. The amount of chelating agent required was determined monitoring the absorbance at 258 nm of Fe^{3+} solution by progressively addition of NTA. Increasing the chelator concentration, in fact, the absorbance grew until showing a plateau which coincided with the molar ratio of 1.5:1 (NTA:Fe(III)). This ratio, which correspond to a small excess in NTA was necessary to ensure the complete chelation of the iron content in the condition adopted for chelation process [10]. The concentration of iron chelate used to carry out the present study is significantly higher than what previously proposed by the authors for treatment of recalcitrant effluent. The reason of that is uniquely connected with practical purpose of measurement. When required, hydrogen peroxide was added into the solution immediately before to switch on the reactor lamps.

2.3. Experimental setup

Three experimental devices which simulated three different light sources were employed. UV-A light was supplied to the solution in a photochemical reactor that was a Pyrex-jacketed thermostatic 2 L vessel (inner diameter 11 cm; height 23 cm) equipped with three black-light blue lamps (Philips TL 8W, 08 FAM) wrapped in three Duran glass tubes with emitted radiation between 350 and 400 nm and maximum at 365 nm [20]. The photon flow was

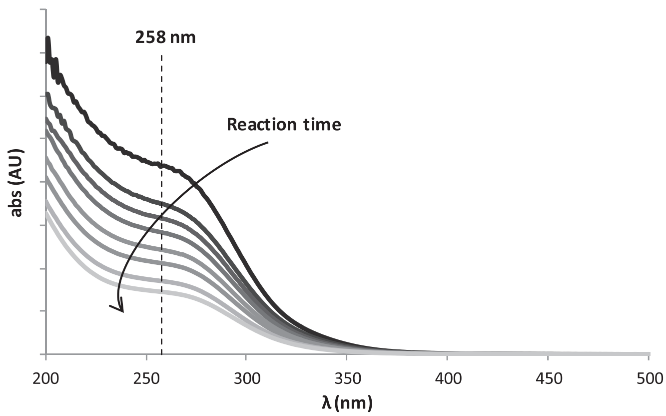

Fig. 1. Evolution of the absorption spectrum because of iron chelate solution instability.

measured with *o*-nitrobenzaldehyde actinometry [21,22] and was 5.05×10^{-6} Einstein s^{-1} at 365 nm. UV-C light was supplied in a photochemical reactor quite similar to the previous but with different lamps. Thus, three fluorescent lamps (Philips TUV 8W, G8T5) wrapped in three quartz tubes, with emitted radiation between 200 and 280 nm, with a maximum of 254 nm were used. The photon flow was measured by chemical actinometry [21] and was 0.94×10^{-5} Einstein s^{-1} at 254 nm. Solar light was simulated with a solar simulator (Solarbox Co.Fo.Me.Gra, 220 v, 50 Hz). The solution was continuously pumped (peristaltic pump Ecoline VC-280 II, Ismatec) into the Solarbox and recirculated back to the reservoir jacketed thermostatic 1 L stirred tank. Inside the Solarbox, a Duran tubular photoreactor (0.078 L) was irradiated by a Xe-lamp of 1 kW (Philips XOP 15-OF 1CT). The photon flow was measured with *o*-Nitrobenzaldehyde actinometry [21,22] and was 2.68×10^{-6} Einstein s^{-1}.

The vessel was covered, in all the cases explained, with aluminum foil to avoid loss of photons and personal damage. During the runs, the temperature was kept constant with a thermostatic bath (Haake C-40) by circulating the water through the jacket around the reactor. Good mixing was provided using a magnetic stirrer. When hydrogen peroxide was added, UV and Xe lamps were switched on. The system was left to react during 2 h even after the total consumption of the hydrogen peroxide in order to evaluate the extra effect on chelates stability for organic radical eventually produced.

2.4. Analytical determination

Fe(III)-NTA stability was determined registering the absorbance of the 0.20 μm filtered samples at 258 nm using a UV/vis spectrophotometer (PerkinElmer Lambda 20). During the reaction the instability phenomena arisen were monitored registering the evolution of the solution absorption spectrum. Because the decomposition of the complexes due to the stress caused by the applied conditions, iron was released from the chelator structure and a reduction of the absorbance was observed as shown in Fig. 1.

Total organic carbon determination, as NPOC (Non-Purgeable Organic Carbon), was carried out in a TOC-VCSN TOC analyzer. Hydrogen peroxide was measured by spectrophotometric method using ammonium metavanadate at 450 nm [23]. Hydrogen peroxide also absorbs at 258 nm but his contribution at the considered concentration was totally insignificant compared to the intensity of the peak registered for Fe(III)-NTA chelates (0.2% of the initial absorbance exhibited by the chelates solution). In this regard we consider that the presence of oxidant did not compromise the monitoring of chelates solution stability.

2.5. Methodology

The effects produced on chelate solution stability by the variation of different operating parameters have been evaluated separately as well as synergistic effects.

The parameters that have been varied were:

- The temperature in dark as well as during the irradiation with UV-A and also after addition of hydrogen peroxide (0.59 mM);
- The hydrogen peroxide doses (0.59 mM, 1.18 mM and 2.94 mM) at standard temperature (25 °C) and under UV-A irradiation;
- The source of irradiation during oxidation by adding specific hydrogen peroxide dose (0.59 mM) and at standard temperature (25 °C).

Effects on chelates solution stability could be also produced depending of the concentration of iron and NTA adopted. However, these two concentrations should be fixed in order to establish a good compromise between process efficiency and environmental safeguard. In previous study [10], Fe^{3+} was fixed to 0.089 mM to ensure a considerable reaction kinetic even if lower than conventional photo-Fenton as consequence of the effect of chelation. This concentration was also considered the optimum to make possible the reuse of the effluent in agriculture without excessive requirement of NTA content. The amount of chelator was instead determined to ensure the complete chelation of the iron content (1.5:1 NTA:Fe(III)). Under photochemical stress the stability would be probably compromised as much as lower is the concentration of the chelates. The moles of photons available are in fact independent of the characterization of the solution. Thus, the moles of photons per mol of chelates in the unit time will be lower when increasing the concentration of chelates. Under photochemical and oxidative stress, instead, the worse scenario would occur in correspondence of the higher concentration of chelates used. In this condition, the amount of Fe(III)-NTA would influence the stability of the chelate solution in reason of the more or less enhancement of the kinetic order rate of the photo-Fenton reaction.

In this study, pseudo-first order kinetic constants have been calculated for all the curves of absorbance reduction in order to better compare the obtained results.

3. Results and discussions

3.1. Effect of temperature, UV-A exposure and H_2O_2

The effect that heating can produce on metal chelate solution, reflected in the change of the stability constant value, is attributable to the structural change of the functional groups. Since the heating is not enough to change the ionic type of reaction no significant effects would be observed. On the other hand, ionic or Coulombic effect will be observed in charge and charge distribution of the anions, and in the charge and the radius of cations. When that happens the most profound change is in the nature of the double bond of the carbons. Then, the mesomeric effect of resonance structure can be responsible of catalyst decomposition and losing of its activity [24,25].

The knowledge of the effects produced by the temperature on the stability of the iron chelate solution is important for correctly determine the set up of experimental temperature as also for an adequate control during the storage of the solution before its utilization.

As Fig. 2 shows, during two hours in which the solution was kept at constant temperature, no changes of absorbance were registered. These results are able to demonstrate as in the tested range, the temperature did not produce the arisen of instability phenomena.

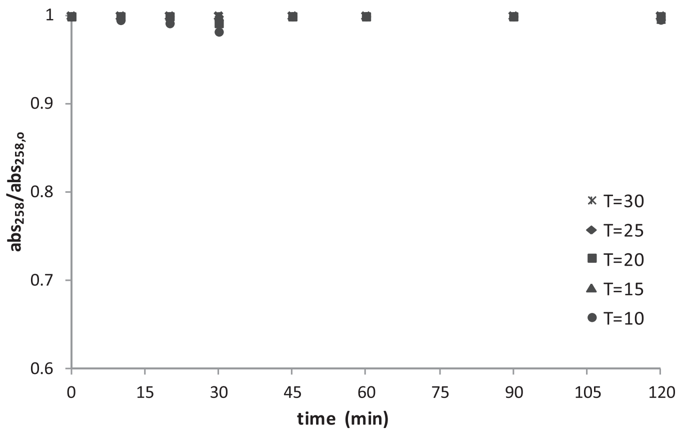

Fig. 2. Variation of the intensity of the absorption peak during two hours at different temperatures.

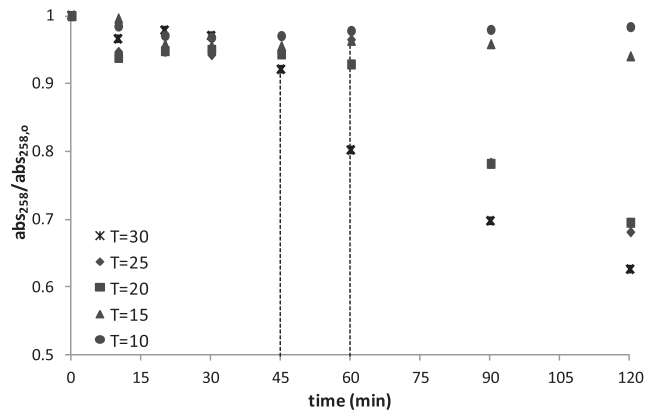

Fig. 4. Evaluation of the iron chelate stability under UV-A irradiation and different temperature (T = 10–30 °C).

More interesting could be the monitoring of the solution stability under combined effect of aging and inconstant temperature. This information is, in fact, very useful in order to better implement the wastewater treatment plant's management system. In this regard, the evolution of the absorption spectrum was monitored during 9 days of storage at room temperature without specific control of temperature (T = 23–32 °C).

In Fig. 3, the absorption spectrums show as, the reduction of the absorbance registered at 258 nm after 9 days of storage without temperature control was completely insignificant (≈3% absorbance reduction). The results obtained were able to demonstrate as, under natural conditions of temperature any system of temperature control is not required to keep stable the chelate solution during the storage.

Different response in stability was expected under irradiation strain. Thus, the stability of iron chelate solution was monitored during two hours under UV-A irradiation and temperature control. The changes in absorbance at 258 nm exhibited by the solution under UV-A irradiation and constant temperature are shown in Fig. 4. The results highlight as under photons transfer the role of the temperature control completely changes. In fact, when UV-A radiation was applied, keeping the temperature in the lower values tested allowed to extend the chelates lifetime.

When temperature was kept between 10 and 15 °C, no reduction of chelate content was essentially arisen during two hours of irradiation. The curve of absorbance reduction, in fact, showed a pseudo-first order kinetic constant almost null (k = 0.0007 min^{-1}). On the other hand, when under irradiation the temperature of the solution was kept between 20 and 25 °C it was possible to observe two different steps in the stability of the chelates. Until 60 min of irradiation, in fact, the absorbance of the solution at 258 nm was almost constant (k = 0.001 min^{-1}). Since this moment and during one more hour of irradiation, the trend radically changed. Thus, a reduction in chelate content was gradually registered revealing the beginning of the complexes damage. This evidence was also confirmed by the appreciable increment of the pseudo-first order kinetic constant calculated for the second segment of the curve (k = 0.0025 min^{-1}). Similarly to this behavior, when the temperature was risen at 30 °C, instability phenomena were sooner arisen. The second segment of the curve of absorbance reduction was, in fact, recognizable earlier than what observed a lower temperature. Thus, also in this case two different segments could be clearly identified, the first one corresponding to the first 45 min of irradiation (k = 0.001 min^{-1}) and the second one representative of the last 75 min of irradiation (k = 0.0026 min^{-1}). Thus, even if the temperature cannot directly influence the achievement of instability phenomena in chelate solution, its control allows extending the lifetime of the catalyst. The release of iron will start as sooner as higher the temperature is. Since it starts, the chelates solution's decay followed a similar trend. This similarity is remarkable for the almost parallel curves of absorbance reduction which, in the second segment, showed almost the same pseudo-first order kinetic constants. Under the considered condition no instability phenomena was achieved before 45 min of UV-A radiation. Nevertheless, no more than approximately 40% of the chelates resulted decomposed under the considered operating conditions. The effect of direct photolysis on solution mineralization was also monitored (Fig. 5).

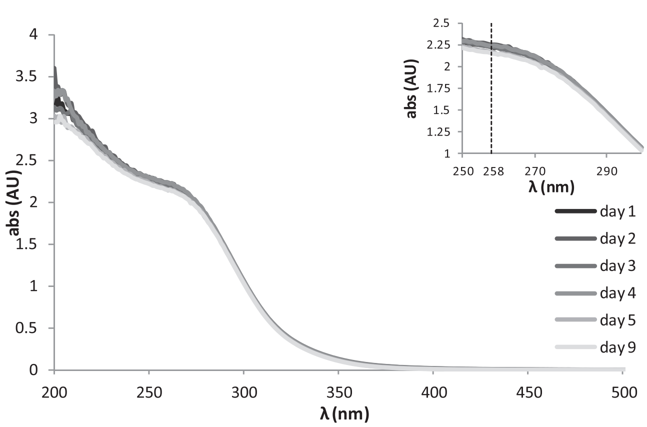

Fig. 3. Evaluation of the iron chelate stability of the solution kept at room temperature during 9 days.

The mineralization achieved was almost the same under all the considered conditions being efficiency variable between 11 and 16%. The trend was practically the same in the whole range of temperatures tested. All the curves showed a first step in which the mineralization was not yet started followed by a second one in which a small NPOC removal was gradually achieved. After correlation of this result with what shown in the previous figure, additional discussion can be done. During the first part of the reaction the photons transferred, in almost all the temperature test range, were not able to produce the breakage of the chelates bonds and no NPOC removals could be achieved. Then, by an intramolecular photoredox process, which leads to the chelates destruction, ferrous ion and organic radicals from the ligands were formed [26]. A small mineralization of the solution could be then achieved [26,27]. Because the APCAs like NTA do not absorb light in the range of study, the direct photolysis might be negligible [28]. Thus the mineralization obtained can be entirely ascribable to the organic radicals produced. By knowledge obtained by published works about the

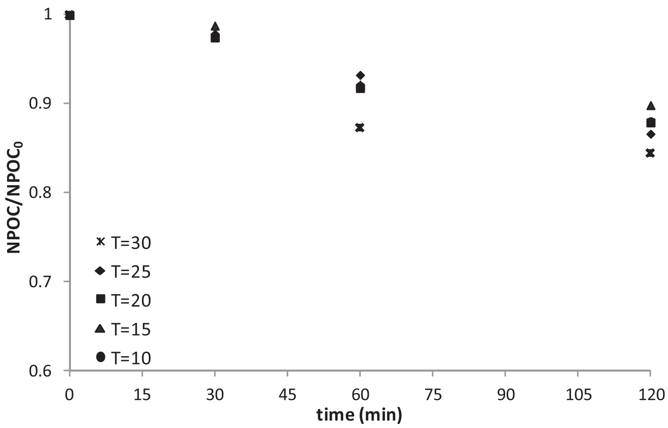

Fig. 5. Effect of mineralization by direct photolysis on iron chelate solution under UV-A irradiation and different temperature (T = 10–30 °C).

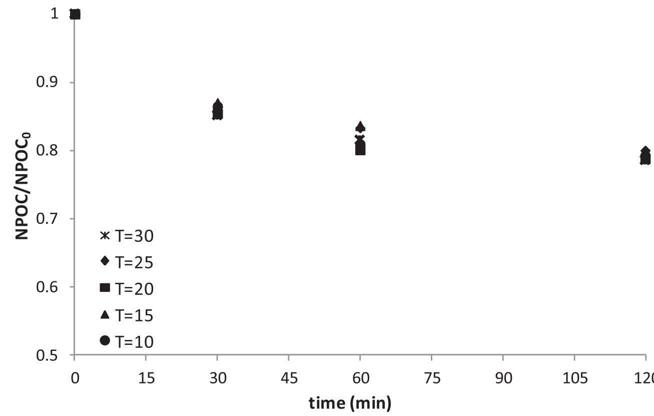

Fig. 7. Mineralization of iron chelate solution under oxidation with UV-A irradiation and different temperature ($[H_2O_2]_0$ = 0.59 mM, T = 10–30 °C).

photochemical degradation of Fe(III) nitrilotriacetate solution, the mayor photoproducts expected are Fe(II), iminodiacetic acid (IDA), formaldehyde and CO_2 [18,29]. At lower temperatures, even if minimum reduction in absorbance was observed, almost 10% of mineralization was obtained. This result can be explained taking into account the greater content of free chelator due to the different molar concentration adopted for NTA and Fe^{3+} (1.5:1 NTA:Fe^{3+}). Thus, the minor production of organic radicals could be equally responsible of the attack to free ligands already present, which degradation was observable in NPOC removal but did not produce any effect in absorbance reduction.

The effect of the temperature was also evaluated under UV-A irradiation of iron chelate solution by adding 0.59 mM of hydrogen peroxide. As extra effect, due to the oxidative stress, a much higher contribution on chelate decomposition was expected.

Looking at the results showed in Fig. 6 is possible to observe as, differently of what illustrated for the direct photolysis of the solution, the presence of H_2O_2 involved the chelates decomposition since the beginning of the irradiation. An initial faster reduction in chelate content was already achieved in the first 30 min of reaction when the registered drop in absorbance was between 26% at 10 °C and 40% at 30 °C. Finally, after 120 min of reaction, the global reduction of ligand content was variable between 42% and 60% at 10 °C and 30 °C, respectively. Thus, it seems clear as after the addition of the oxidant, an adequate control of the temperature could be really useful to extend the lifetime of the chelates. Remarkable is the experimental evidence of total H_2O_2 consumption achieved after only 10 min. of reaction for the whole analyzed conditions.

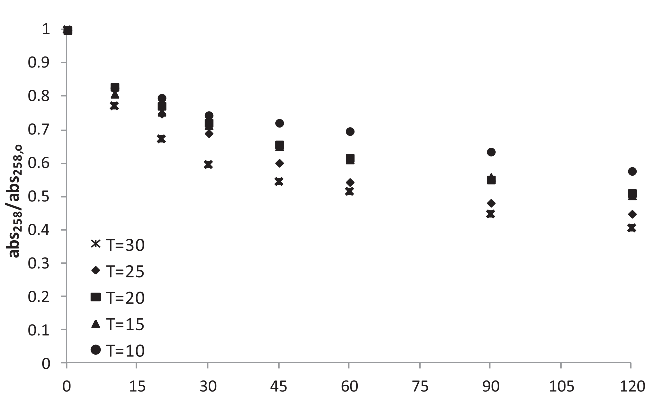

Fig. 6. Evaluation of the iron chelate stability under oxidation with UV-A irradiation and different temperature ($[H_2O_2]_0$ = 0.59 mM, T = 10–30 °C).

The kinetics exhibited in chelates decomposition make possible identifying three range of temperature within which the trend was comparable. The calculated pseudo-first order kinetic constants were, in fact, respectively, $k = 0.0056\ min^{-1}$ for temperature set at 10 °C, $k = 0.0067\ min^{-1}$ for T = 15–25 °C and $k = 0.0091\ min^{-1}$ for T = 30 °C. The mineralization of Fe(III)-NTA solution obtained under UV-A irradiation and after adding 0.59 mM of H_2O_2 are shown in Fig. 7.

As effect of the H_2O_2 addition, the mineralization of the solution is also appreciable since the beginning of the reaction. The hydroxyl radicals produced quickly attacked the chelates molecules producing the breakage of the bonds of the Fe(III)-NTA complexes. As effect of the chelates decomposition, confirmed by the reduction of the absorbance at 258 nm, the correspondent amount of free chelator obtained was made available for mineralization. Differently from what registered in absence of oxidant, the mineralization curve of the solution did not show any initial segment essentially horizontal confirming the instantaneous occurrence of breakage and then mineralization of the chelates. It appears also clear as the amount of oxidant was totally inadequate to achieve high levels of efficiencies. After 30 min of reaction only the 15% of mineralization was achieved. Taking into account the total H_2O_2 consumption at 10 min of reaction and comparing this data with the much more smaller efficiency obtained under the same irradiation dose in absence of oxidant (≈1%), it is reasonable to ascribe this efficiency to the oxidative hydroxyl radicals activity. Since this time and until the end of the experiment, the extra contribution on mineralization was fixed at 5–6% of total carbon removal. This additional removal can be then ascribable to the presence of organic radicals originated from the oxidation of the free NTA. In fact, at wavelength longer than 345 nm, a redox process between Fe(III) and the carboxylate group of the ligand takes place. This process gave way to the production of Fe(II) and $R'CH_2CO_2$ which in turn undergone a decarboxylation giving rise to $R'CH_2^{\bullet}$. This radical chain, united with the direct photolysis of the solution, was suppose to be the responsible of the additional mineralization achieved [27].

3.2. *Effect of H_2O_2 doses*

At standard temperature (T = 25 °C) the effect of hydrogen peroxide concentration was evaluated. In order to quantify the effect of the H_2O_2 dose on the instability of iron chelates solution, different Fe^{3+}:H_2O_2 ratios were adopted. In Fig. 8, is shown the reduction of chelates content occurred into the irradiated solution with UV-A light using the Fe^{3+}:H_2O_2 ratios of 1:1, 1:2 and 1:5, respectively.

Obviously, the effect on chelate stability was much destructive as higher was the concentration of oxidant employed. The

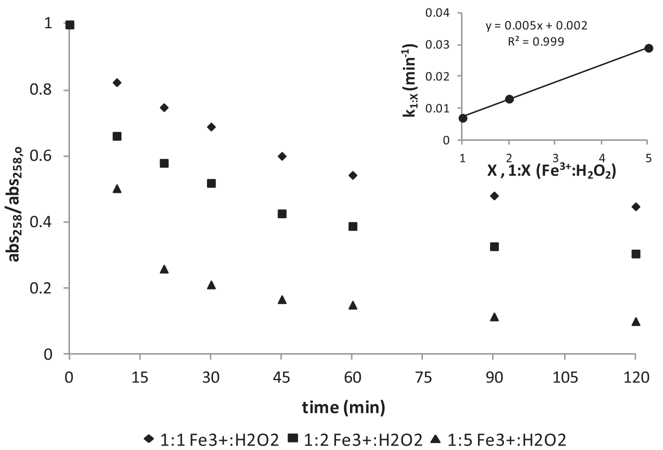

Fig. 8. Evaluation of the iron chelate stability under oxidation with UV-A irradiation at standard temperature (T= 25 °C) and different Fe^{3+}:H_2O_2 ratios ($[Fe^{3+}]_0$ = 0.36 mM; $[H_2O_2]_0$ = 0.59 mM, 1.18 mM, 2.94 mM).

knowledge of the full extent of this effect could help in prediction of the efficiency reduction of Fe(III)-NTA as catalyst. As previously occurred, the complete hydrogen peroxide consumption was obtained in the first 10 min of reaction for all the conditions analyzed. As observable in the top of the figure, in this period when the curves showed a considerably higher slope, the pseudo-first order kinetic constants appeared almost proportionally to the increasing of oxidant concentrations ($k_{1:1}$ = 0.007 min^{-1}, $k_{1:2}$ = 0.013 min^{-1}, $k_{1:5}$ = 0.029 min^{-1}). The quick complete consumption of the oxidant for the whole doses employed could have been occurred for the insufficient amount of oxidant as well or, in some cases, for its excess by reducing the oxidation rate of the Fenton's process [30,31]. Anyway, since the hydrogen peroxide was completely exhausted, a stronger reduction in chelates content was still observed and it was much more significant as higher the initial hydrogen peroxide concentration was. Once again, this result could be related with the higher production of organic radicals generated for decomposition of the Fe(III)-NTA chelates. Finally, after almost 20 min from the beginning of the reaction, the kinetic reaction drastically dropped as obviousness of the consumption of the organic radicals produced. The final reduction in chelates content (after 120 min of reaction) settled at 90%, 69%, and 55% of the initial value for the Fe^{3+}:H_2O_2 ratios of 1:5, 1:2 and 1:1 respectively.

In the previous study of the authors, photo-Fenton like at neutral pH catalyzed by Fe(III)-NTA chelates was applied for sulfamethoxazole removal. Using the same NTA:Fe^{3+} molar ratio adopted in the present study (1.5:1 NTA:Fe^{3+}) but by adding 0.29 mM of H_2O_2 (1:2 Fe^{3+}:H_2O_2), the reduction of iron content started only after 45 min of irradiation. This different result can be explained taking into account the effect of the competition established between the compounds for reaction with the available non-selective HO$^\bullet$ [10]. Thus, the amount of radicals made really available for reaction with the chelates was reduced and the lifetimes of the chelates could be extended. Finally, even though the response of the chelates can change according with the complexity of the system, the information got in the present study is able to make more understandable how the parameters influence the stability of the catalyst.

In Fig. 9, are shown the curves of NPOC removal obtained by adding the tested H_2O_2 doses. The efficiency achieved for solution mineralization showed a progressive increment according to the increment of the hydrogen peroxide dose applied (from 20% to 44% when increasing H_2O_2 by five times). Besides, the curves showed a changes in the rate of the reaction occurred at the total consumption of the hydrogen peroxide allowing identify two

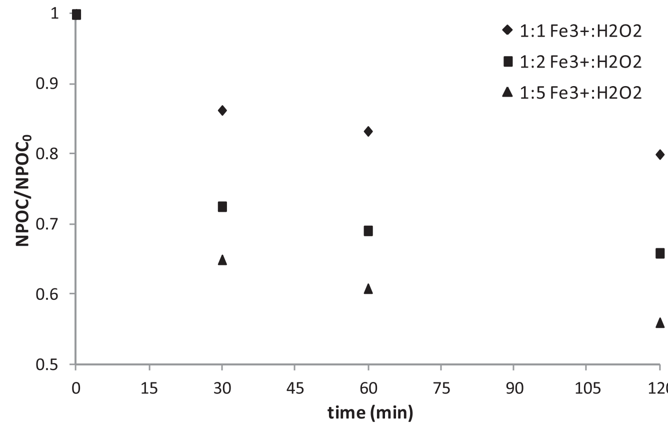

Fig. 9. Mineralization of iron chelate solution under oxidation with UV-A irradiation at standard temperature (T=25 °C) and different Fe^{3+}:H_2O_2 ratios ($[Fe^{3+}]_0$ = 0.36 mM; $[H_2O_2]_0$ = 0.59 mM, 1.18 mM, 2.94 mM).

different steps of the reaction. In the first one, hydroxyl radicals and organic radicals were both responsible for the mineralization of the solution followed by another step in which the extra efficiency was ascribable to the action of the only organic radicals.

3.3. *Effect of UV-light exposure*

Because the maximum absorption of chelate solution was registered at 258 nm, the range of wavelength of radiation emitted from the lamp implies effects strongly different. Thus, the contribution of light on chelate stability is obviously dependent of the source used to transferring the photons.

Three light sources were employed to study their contribution on chelates stability during the irradiation after adding 0.59 mM of hydrogen peroxide (Fig. 10).

It was expected that the higher effect in terms of chelate decomposition would have been obtained by UV-C irradiation which wavelength of emitted radiation (254 nm) is the closest to the maximum absorbance of the solution (258 nm). Moreover, the emission spectrum of UV-C lamps is also included in the range of absorbance of H_2O_2 (<310 nm) that involves a higher HO$^\bullet$ production. The experimental result remarks as, also in this case, the complete hydrogen peroxide consumption was achieved after only 10 min since the beginning of the irradiation. In this case the kinetic rate followed by the reaction assumed a pseudo-first order kinetic constant of 0.042 min^{-1} and more than 70% of Fe(III)-NTA chelates were destroyed in only 10 min of reaction. Afterwards, the kinetic

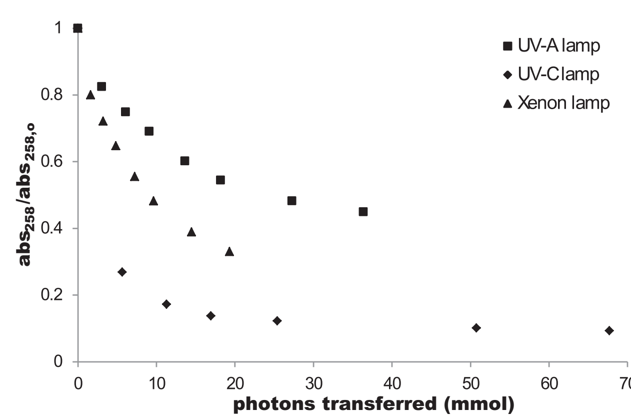

Fig. 10. Evaluation of the iron chelate stability under oxidation with $[H_2O_2]_0$ = 0.59 mM at standard temperature (T=25 °C) under different source of UV irradiation.

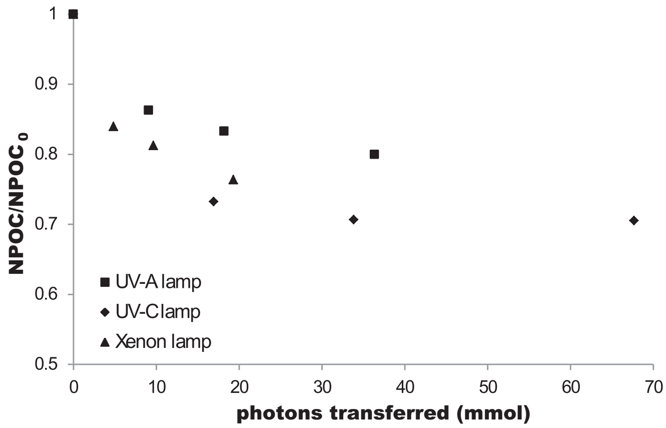

Fig. 11. Mineralization if iron chelate solution under oxidation with $[H_2O_2]_0$ = 0.59 mM at standard temperature (T = 25 °C) under different source of UV irradiation.

reaction showed a strong reduction when the chelates decomposition was entirely attributable to the only action of the organic radicals. Thus, the reaction totally ended after 30 min of irradiation (which correspond to ≈17 mmol of photons transferred to the solution) when less than 10% of the initial chelates contents remained available.

On the other hand, a great similarity was observed between the results exhibited when UV-A lamps and solar simulator were used to irradiate the solution. The Xenon lamp, in fact, emits in a wider range of wavelengths (>280 nm) than the UV-A lamps but with intensity sensibly lower than them which emission is instead totally concentrated at 356 nm. The reactions followed a kinetics rate which the pseudo-first order kinetic constants assumed the values of 0.007 and 0.008 min^{-1}, respectively. After the total hydrogen peroxide consumption (at 10 min) the kinetic slowly reduced overtime reaction. The wider emission spectrum of the Xenon lamp was probably responsible of the higher instability arisen with respect to what happened when UV-A lamps were employed. After 120 min of irradiation, in fact, the 67% of chelates destruction was caused but a 55% was instead obtained under UV-A irradiation with a global amount of photons transferred of almost 19 and 36 mmol, respectively. It seems clear as, overlooking in this context the characteristic of contamination, UV-A light could represent the more adequate choice of irradiation to better preserve the chelates during the reaction.

Finally, the efficiency obtained in terms of solution mineralization is shown in Fig. 11. No correlation between the higher level of Fe(III)-NTA decomposition and solution mineralization was found under UV-C irradiation. The efficiency registered for the solution mineralization was of almost 30% which was not so higher if compared to what instead obtained in the other two cases analyzed (20% and 24% with UV-A and Xenon lamps, respectively). Thus, after the total consumption of H_2O_2, the organic radicals generated were strongly responsible for the breakage of the bonds in chelates structure but their contribution was not enough to produce the mineralization of the effluent. Furthermore, the photochemical activity of the organic radicals could not allow the achievement of a higher mineralization. Therefore, the use of such a high energetic light could be more counterproductive than useful in terms of prolonging the lifetime of the chelates.

4. Conclusions

An analysis of the stability of the chelate solution under different combination of the most important operating parameters that influence photo-Fenton like at neutral pH was carried out. Three operating parameters were considered as stress factor for the chelate solution (i.e., photochemical stress, oxidative stress and thermal stress).

It was found out that the control of temperature is unnecessary if performed in absence of any other stress factors for the solution. During 9 days without temperature control, no changes were observed in the absorbance exhibited by the chelate solution which demonstrates a good stability of the complexes under aging.

Under UV-A irradiation the chelates solution showed a temporary stability before exhibiting a gradual damage and subsequent iron release. Nevertheless, the possibility of delaying the beginning of the instability phenomena by temperature control was demonstrated. In fact, the decomposition of chelates started as soon as higher the temperature of the solution was kept. In spite of that, the release of iron from the structure of the complex was completely avoided during two hours of irradiation when keeping the temperature at 10–15 °C. Particularly interesting is the evidence that shows no release of iron before 45 min of irradiation under the whole temperature test range. Under UV-A irradiation a slow mineralization of the solution was also achieved (≤16%). Likewise, NPOC removal curves showed a first step in which the solution remained stable followed by a gradual decline due to the action of the organic radicals produced by the breakage of the chelates.

By combining photochemical and oxidative stresses, the chelate decomposition with subsequent iron release was unavoidable. Thus, by adding H_2O_2 (0.59 mM) the absorbance reduction curves of the solution showed a gradual decline since the beginning of the irradiation. Regardless, once again by controlling the temperature solution was still possible the achievement of a chelates lifetime extension (from 60% of reduction to 42% in two hours turning the temperature down 20 °C). Besides, similarly to what observed in chelates content reduction, the mineralization of the solution started simultaneously with the beginning of the irradiation. Thus, the extra oxidation attributable to the generation of hydroxyl radicals allowed an only slight enhancement in NPOC removal (≤20%).

The effect on chelates stability of different hydrogen peroxides doses was also considered. A direct proportional correlation between the hydrogen peroxide dose and the destruction of Fe(III)-NTA was found out. Also the efficiency in mineralization showed a progressive increment according to the increment of the hydrogen peroxide dose applied (from 20% to 44% when increasing H_2O_2 by five times).

The influence of the emission spectrum of the lamps employed for irradiation was finally confirmed. As it was expected UV-C lamps were the most unfavorable for applications in photo-Fenton like at neutral pH catalysed by iron chelates. The solution, in fact, suffered an unbearable stress because the proximity of its peak absorbance wavelength to the peak emission wavelength of the UV-C lamps. More than 90% of reduction in chelates content was, in fact, registered after only 30 min of UV-C irradiation by adding 0.59 mM H_2O_2. In spite of that, 55% and 67% of reduction of the chelates available for the reaction was registered after two hours under irradiation with UV-A and Xe lamps by adding 0.59 mM H_2O_2. The wider range of Xenon lamp emission wavelength than UV-A lamps was responsible of the higher instability produced in the chelates solution during the exposure. Finally, to ensure as long as possible the preservation of the chelates and the subsequent catalytic activity of the solution, UV-A irradiation could be recommended.

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